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Biologically mediated dissolution of volcanic glass in seawater

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Abstract

We studied the effects of biological mediation on the dissolution of basaltic glass in seawater. Experiments with typical seawater microbial populations were contrasted with a sterile control, and reactions were monitored chemically and isotopically. Biologically mediated experiments produce twice the mass of authigenic phases than abiotic experiments and the phases are different. Abiotic alteration of glass dissolves basaltic Si and Ca and scavenges seawater Mg, while biotic alteration removes Ca from seawater. Such opposing behavior of Ca and Mg in biotic and abiotic alteration of basaltic glass may have important implications for the carbon cycle and the exchange processes between ocean crust and seawater. $^{87}Sr/^{86}Sr$ data of glass and alteration products suggest that biological mediation enhances both the diffusion of seawater Sr into glass by a factor of 3–4, and the dissolution of basaltic Sr into seawater by a factor of 20–40. The dependence of chemical exchange processes between seawater and glass on biological activity implies that chemical fluxes from water–rock interaction at low temperatures may change as life on Earth evolves.

Keywords: biogeochemistry; volcanic glass; water–rock interaction

1. Introduction

Low-temperature alteration of volcanic materials in the oceans plays an important role in controlling the chemical balance between seawater, ocean crust, near-arc sediments, arc magmatic systems and the earth's mantle. Volcanic glass plays a particularly important role in these processes, due to its chemical instability and high abundance in the marine environment [1]. Recently, it has become clear that microbial processes mediate alteration of volcanic material in the oceans. In particular, it has been pointed out that microbes may be involved in the dissolution of volcanic glass [2–5] whereby microbes have been identified on glass surfaces well into the oceanic crust [5–7]. Furthermore, bacteria may be also invoked in the origin of a variety of mineral deposits produced by hydrothermal solutions [8,9]. The chemical effects of these chemical

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and biological processes are poorly understood. In this paper, we address the following questions: (1) Is microbially mediated dissolution of glass in seawater different from abiotic alteration? (2) What are the bulk chemical effects? (3) Are there any differences in rate constants for biotic and abiotic dissolution?

We carried out experiments for the dissolution of basaltic glass in seawater. In particular, we conducted glass dissolution experiments in seawater containing natural near-surface ocean microbial populations, and in sterile seawater. We monitored dissolution progress by analyzing the SiO_2 inventory of solutions, and we analyzed starting materials and run products for major element geochemistry and $^{87}Sr/^{86}Sr$ isotope ratios.

2. Previous work

Most previous work on glass alteration focuses on petrography and microprobe analyses of submarine glass and palagonite, its primary alteration product (e.g. [10,11]. Morgenstein and Riley [12] propose that glass dissolution involves the diffusive penetration of water into the fresh glass and the formation of an immobile product layer whereby palagonite is considered to be the result of an incongruent dissolution–chemical exchange process. However, Crovisier et al. [11] make the case that glass alteration is a congruent dissolution process and they interpret the sharp interface between glass and palagonite as a front of complete dissolution and re-precipitation of glass. Micro-cracks or channels on glass surfaces at the glass–palagonite interface are interpreted either as a physical step during inorganic dissolution of glass [11,12] or as a product of biological activity [2–5]. A suggested biochemical mechanism for localized dissolution of glass is that colonizing bacteria produce acidic (or alkaline) substances which locally change the pH and hence advance dissolution of glass [3]. Recent studies show that corrosion damage to glass correlates with in-situ observations of microbes within rock samples drilled from depths greater than 100 m in the oceanic crust [5–7], and experimental investigations demonstrate that microbially caused corrosion damage can be simulated in the laboratory. These experiments include microbial cultures from natural hyaloclastites [13], natural seawater [14], and marine cyanobacteria [14]. Corrosion pits and grooves observed in biological experiments did not form in sterile controls [14].

All existing data suggest that glass alteration is indeed a combination of biotic and abiotic processes and analytical studies of natural glass and its alteration assemblages apparently reflect both processes. These studies show that glass alteration in nature involves mobilization of a large fraction of its chemical inventory, but much of this material is deposited locally in pore spaces between glass fragments (e.g. [10]). Ti and Fe tend to behave conservatively and become passively enriched in palagonite, the alteration product of glass. Most other elements display variable degrees of mobility. The strongest losses are for Na, but they are significant for Ca as well. Meteoric glass dissolution results in a near-total loss of K_2O, while submarine alteration generally displays a gain in K_2O. Much of the dissolved inventory is deposited in pore spaces between glass fragments. But there are also significant fluxes of elements, in particular K, Rb, and Cs, between glass-rich volcaniclastic rock and seawater [1]. Isotopic analysis of $^{87}Sr/^{86}Sr$ in glass and palagonite suggests that the net fluxes of Sr between seawater and basalt are relatively small, while the exchange rates are high, whereby large quantities of basalt Sr are contributed to seawater and much seawater Sr is contributed to palagonite [1].

3. Experimental setup and methods

The closed-loop flow-through reactor used in this study is made of Teflon (PFE) components and illustrated in Fig. 1. Experiments were carried out at room temperature (20–24ºC), under ambient laboratory light conditions (indirect day light/no night illumination), with the exception of Experiment 7 that was placed into darkness for the last 238 days. No efforts were made to buffer the oxygen fugacity. Experiments lasted between 314 days (Exp. 6) and 583 days (Exp. 7). A peristaltic pump circulated about 10 l of water per day from a 50-l polyethylene water reservoir through the reactor with two successive beds of 75 g of glass sand each. These glass charges, as well as some polished glass plates, were positioned on top of Teflon frittes within the

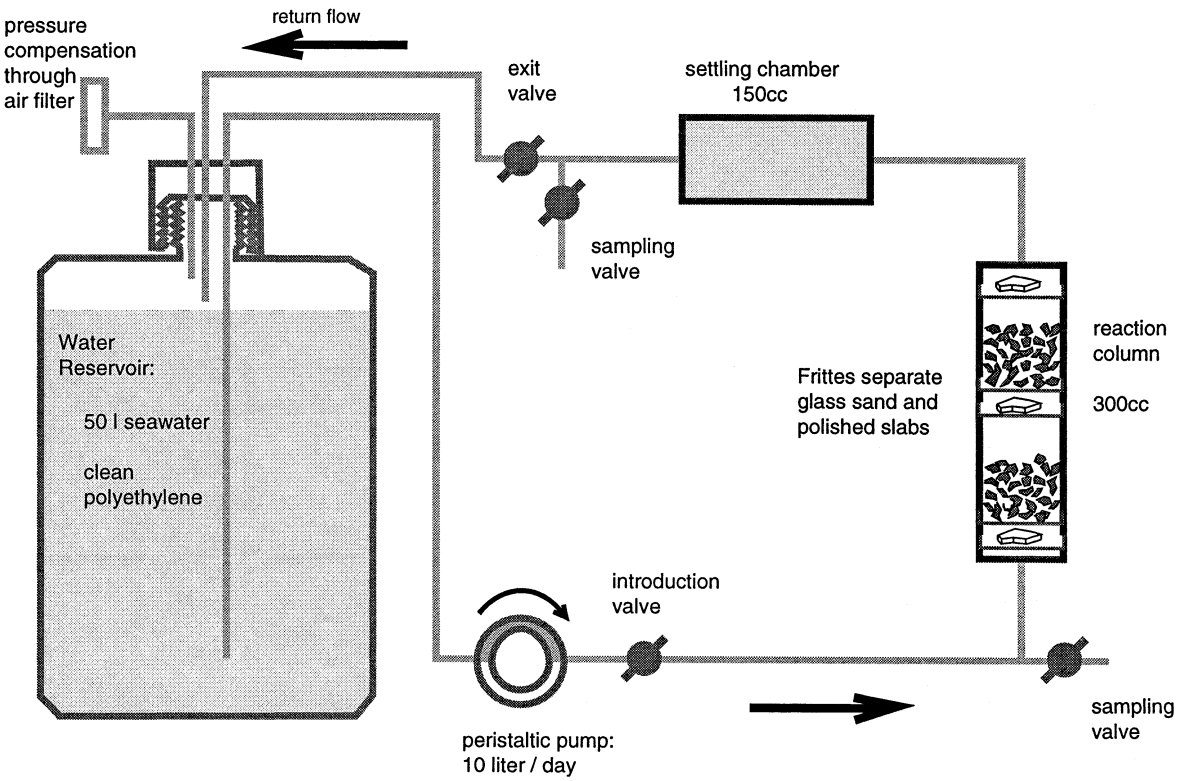

Fig. 1. Schematic drawing of the flow-through reactor used for our experiments. All components are made of Teflon, with the exception of the water container made of linear polyethylene and the Pharmed® tubing in the peristaltic pump. The latter pumps about 10 l of seawater per day from a 50-l reservoir, through a bed of about 150 g of glass sand that is situated on top of frittes in the reaction column.

reactor column segment (Fig. 1). Pressure compensation of the system was facilitated through an air vent with a 1-μm filter at the top of the water container. Experiments 5 and 6 used basalt glass, fused from a homogenized tholeiitic basalt powder from the Loihi seamount, Hawaii. Experiment 7 used a glass quenched from an active tholeiitic lava flow from Pu'u Oo, Hawaii (Table 1). The fresh glass was crushed to a grain size of about 1–4 mm in diameter with a surface area of approx. 0.01 m^2/g, using an extrapolation of BET measurements [15] on a series of successively finer fractions. The seawater was taken from the laboratory seawater supply of Scripps Institution of Oceanography, approximately 100 m offshore, pumped mostly through polyethylene pipes and filtered sand. This water was not further filtered for our experiments and thus retained a portion of its microbial population. The apparatus for the abiotic experiment was sterilized by autoclaving separately the seawater and the (dry) reaction column. The sterilization of the seawater container was gauged with a test culture of thermophilic bacteria confined in a sealed tube, immersed in the seawater, and autoclaved with it. The seawater in all experiments was monitored for Si, pH and biological composition at regular intervals and at the termination of the experiments. Samples for biological studies were also collected from areas of visible growth in the biotic experiments. Samples of biofilm were aseptically taken at the conclusion of each experiment from the inside surface of the glass-packed columns and from the inlet and outlet tubing. Enrichments were made under aerobic conditions and 20°C for heterotrophic, photoautotrophic and chemolithotrophic microorganisms.

Starting materials and run products were characterized with a suite of techniques including the electron microprobe (EMP), scanning electron mi-

Table 1
Major element analyses of starting materials and run products

	Starting materials			Run products (XRF, in wt%)			
	fresh glass (EMP, in wt%)		seawater (μg (el.)/l)	Experiment 5, 451 days duration		Experiment 6, 314 days duration	Experiment 7, 583 days duration
Sediment yield	Experiments 5 and 6	Experiment 7		sediment reactor 255 mg	sediment reservoir <30 mg	sediment reactor 177 mg	sediment reactor 925 mg
SiO_2	48.90	51.42	2.81×10^3	21.50	80.70	6.10	34.70
TiO_2	1.60	2.70	4.79×10^{-3}	0.67	0.15	1.44	1.90
Al_2O_3	10.54	13.57	1.62×10^{-1}	4.00	3.40	8.80	10.20
FeO	10.88	11.86	5.59×10^{-2}	4.64	0.78	9.72	10.01
MgO	17.11	6.43	1.26×10^6	4.70	0.00	30.70	5.80
MnO	0.16	0.17	1.92×10^{-1}	0.07	0.02	0.12	0.11
CaO	8.42	11.06	4.14×10^5	37.40	0.80	0.40	18.30
Na_2O	1.75	2.42	1.08×10^7	0.50	0.47	0.10	1.10
K_2O	0.25	0.46	3.89×10^5	0.02	0.30	0.00	0.28
P_2O_5	0.16	0.27	6.00×10	0.22	0.07	0.16	0.18
Sum	99.77	100.35		73.72	86.69	57.54	82.58

Analytical techniques: EMP = electron microprobe, XRF = X-ray fluorescence; analytical accuracy was monitored through the use of international standards and is generally better than 5%.

croscope with energy dispersive analyzer (SEM–EDS), X-ray fluorescence (XRF, [16]), X-ray diffraction (XRD,) and solid source mass spectrometry ($^{87}Sr/^{86}Sr$) and isotope dilution analysis.

4. Results

4.1. Microbiology

The sterility of Experiment 6 was established in several ways. First, colonies of bacteria did not appear on nutrient marine agar plates streaked with water collected periodically from the flow system of Experiment 6. Second, the water samples from the flow system did not show an increase in particles the size of bacteria as judged with Coulter Counter particle counts. Finally, SEM images corroborated these results and showed exclusively inorganic phases, mostly pyroaurite (Fig. 2A) and some (rare) aragonite. The success in keeping Experiment 6 sterile for 452 days showed that our flow-through reactor provided a biologically closed (axenic) system, and gave strong support to the idea that Experiments 5 and 7 inherited their microbial populations entirely from the seawater used.

Enrichment culture and subsequent isolation of bacteria in samples from the initial biotic flow-through experiment (Exp. 5) revealed a variety of gram-negative heterotrophic bacteria, based on cell morphology, motility, pigmentation and colony characteristics. Samples from Experiment 7, were cultured for Cyanobacteria (photoautotrophs) and oxidative chemolithotrophs such as Thiobacilli, nitrifying bacteria and iron-oxidizers. Isolated chemolithotrophs included a rod-shaped (1.5–1.8 × 1 μm) motile sulfur-oxidizer, and two strains of rod-shaped (one 2.5–4.5 × 1 μm, the other 2.3–3.4 × 1 μm) non-motile ammonia-oxidizers. The Cyanobacteria we obtained include *Spirulina*, *Phormidium*, *Anacystis*, and a sheathed, filamentous strain that is probably either *Anabaena* or *Nostoc*, based on light microscopy.

Altered glass surfaces in Experiments 5 and 7 were covered with patches of biofilm (Fig. 2C, D), that remained attached to the glass even after it was dried. We also found a diverse group of diatoms and radial aggregates of thin aragonite crystals (0.5 × 5 μm needles, probably *Halimeda* [17], Fig. 2B). These aragonite crystals were associated with the biofilm and with the algal mucus in the reservoir of Experiments 5 and 7. Diatoms were abundant in both

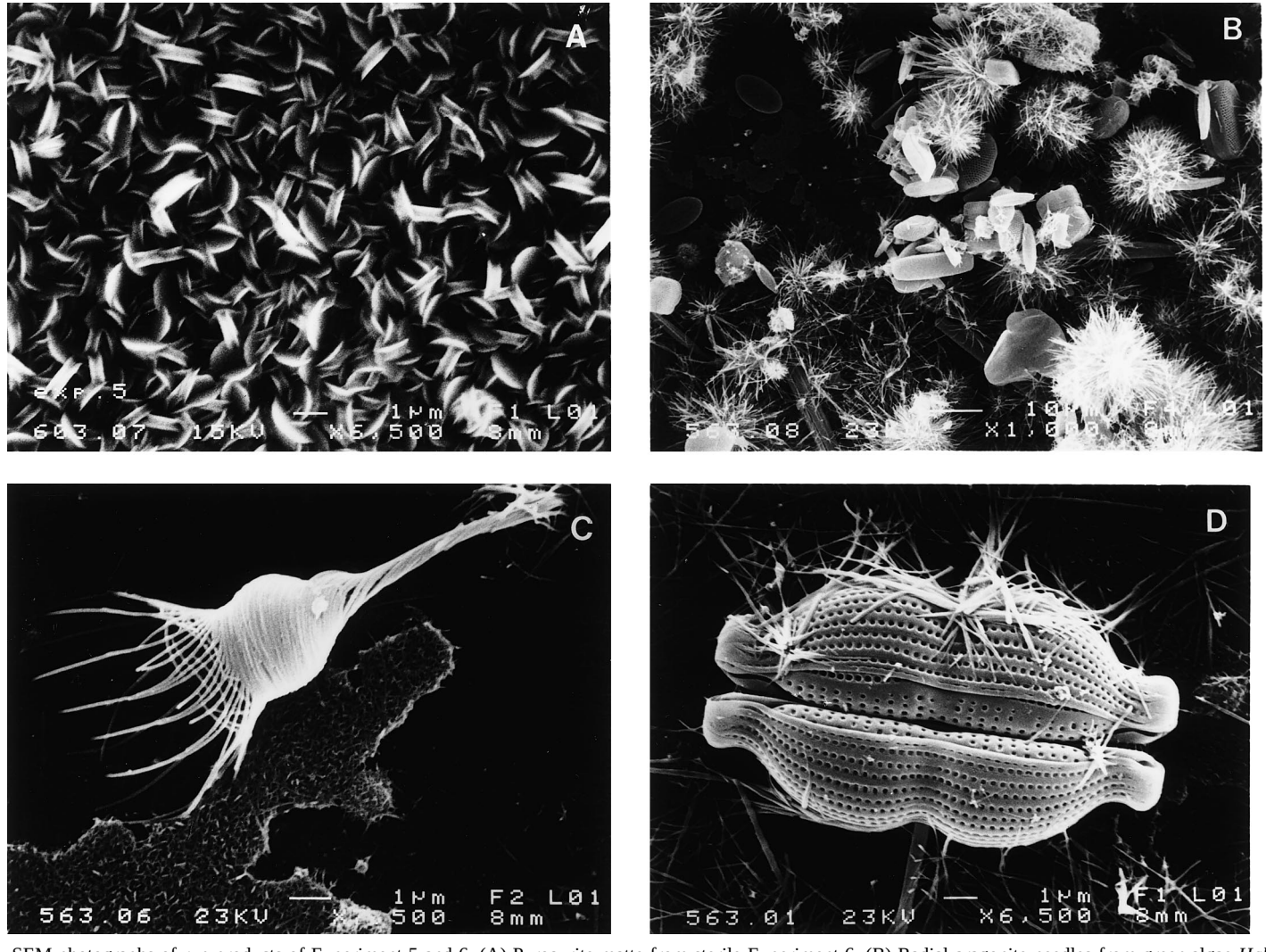

Fig. 2. SEM photographs of run products of Experiment 5 and 6. (A) Pyroaurite-matte from sterile Experiment 6. (B) Radial aragonite needles from green algae *Halimeda* [17] with diatoms from Experiment 5. (C) Coronoflagellate attached to glass with patchy biofilm on black clear glass. (D) Diatom (*Amphora*) in biofilm; note that the biofilm begins to enclose the diatom.

biotic experiments, including many species that are common in California near-shore waters and many of which have a tendency to adhere to sand surfaces (R. Laws, pers. commun.). Some diatom species appear to form 'colonies' that may be associated with biofilms (e.g. *Amphora*, see Fig. 2D).

4.2. Dissolution monitoring and kinetics

Samples were periodically collected from the solutions in the flow reactors and analyzed for pH and SiO_2 inventory (Fig. 3). The pH of the water in the biotic experiments (at 20°C) remained within a range of 8.0–8.5, while that in the sterile experiment was slightly higher (8.7–8.8). The sterile Experiment 6 showed a rapid increase in solution Si from typical surface seawater values to about 75 μmoles/l after 270 days, approximating asymptotically a saturation limit of about 90 μmoles/l (Fig. 2). This behavior is characteristic of a rapid dissolution rate at undersaturated conditions, reaching a precipitation–dissolution equilibrium after about 300 days. From this experiment, we calculate an abiotic dissolution rate of about 500 μmoles (Si) day^{-1} m^{-2}.

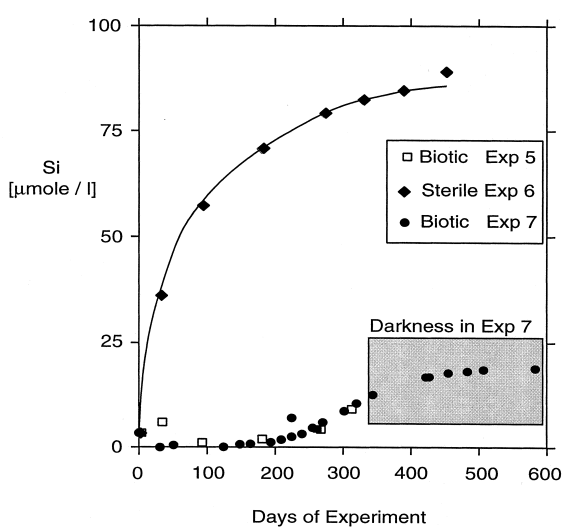

Fig. 3. Solution Si for glass–seawater exchange experiments (Experiments 5–7). The sterile Experiment 6 shows a dissolution behavior indicating a saturation equilibrium at approximately 90 μmoles/l. Experiments 5 and 7 consistently show solution compositions close to the nutrient-depleted surface water used. Some outliers contain unusually high Si, probably from particulates in un-filtered solutions. Abiotic dissolution produces a characteristic dissolution curve where solutions reach dissolution–precipitation equilibrium after 300 days. Intense utilization of Si keeps the Si inventory in Experiments 5 and 7 low.

Experiments 5 and 7 display generally very low solution Si inventories, certainly for the first 200 days (Fig. 3). In fact, the Si inventories drop below values that are characteristic for the surface seawater used (3.5 μmoles Si/l), and they remain low probably due to continued utilization by diatoms. After about 250 days, Si appears to slowly increase until the end of Experiment 5. Experiment 7 follows the results of Experiment 5 and continues its gentle increase. The change towards complete darkness after 345 days in Experiment 7 did not result in a major increase in solution Si, instead, it appears to level off after about 430 days to a dissolution–precipitation equilibrium at about 20 μmoles/l. Most time series include a few outliers to slightly higher values (Fig. 3), that may all be related to the presence of small particles in these (unfiltered) samples.

4.3. Reaction products

Solid reaction products were deposited in the reactor, the tubing, the settling chamber and the sea water reservoir (Fig. 1). Removing these materials quantitatively was difficult because products often stuck to the tubing and container walls. For Experiments 5 and 6, we recovered >80% of the reactor sediments, while we recovered about 95% of the sediments in the reactor and the reservoir of Experiment 7. The greatest amount of alteration product was found in the reactor sediments (Experiment 5: 255 mg; Experiment 6: 177 mg, and Experiment 7: 925 mg). The amount of sediment in the water reservoir was negligible in Experiment 6, was >30 mg of nitric-leached solid residue (analysis in Table 1) in Experiment 5, and was 145 mg (reduced to 69 g after oxidation with concentrated nitric) in Experiment 7.

4.4. Reactor sediments

All experiments produced a surface coating on glass particles and a fine-grained sediment that was deposited throughout the reactor. These sediments and surface coatings were sampled by removing and archiving individual grains of glass and (exposed) polished plates for SEM and EMP analyses.

The fine-grained fraction was sampled by suspension in water, decanting, and filtration. During the suspension process, grain-to-grain abrasion unavoidably removed some of the surface coating and contributed this material to the reactor sediment. Thus, fine-grained reactor sediment and dislodged surface coating cannot be effectively separated in bulk samples. However, more importantly, this process also separated some fine basaltic glass fragments from the larger grains that may be suspended with the fine sediment. This renders the bulk reactor sediment a mixture of loose sediment, surface coatings, and unaltered basalt glass. An estimate of this basalt contribution can be made using SEM and microscopic observations and a chemical mass balance. Visual estimates of microscopic slides suggests a basalt contribution of about 5–10%, <3% and 30–60% for Experiments 5, 6 and 7, respectively. An upper bound for the potential basalt contribution can be made by chemical mass balance, simply by assigning the entire inventory of some of the most lowest abundance elements to basalt (here Na and K). If we assume that *all* of the Na or K in the reactor sediments originates from contaminating basalt fragments, Experiment 5 may include up to 10% basalt in its reactor sediment, Experiment 6 (almost none), and Experiment 7 up to 60%. Both methods provide rather consistent results. The high inventory of Experiment 7 may be due to the fact that we used more aggressive agitation during the separation of fines and because we used a different type of glass (natural vesiculated lava quenched against water). Taking into account the surface area of our basalt glass, the contributions of (contaminant) basalt fractions, and duration of the experiments, we can calculate the minimum production rates of reactor sediments. The biotic Experiments 5 and 7 produced at least 0.48 mg m^{-2} d^{-1}, and 0.43 mg m^{-2} d^{-1} (basalt-free) reactor sediment, approximately twice as much as the abiotic rate (0.25 mg m^{-2} d^{-1}).

X-ray diffraction data, microprobe analyses and XRF analyses (Table 1) suggest that the reaction product of the abiotic Experiment 6 largely consists of pyroaurite, a Mg-rich silicate layer with a brucite structure ($Mg_6Fe_2CO_3(OH)_{16}\cdot H_2O$). Pyroaurite formed a continuous thin layer on the glass (Fig. 2A) quite similar to those seen previously in (abiotic) experiments [18]. The pyroaurite layers tend to break and peel off after the samples were dried in air. In the altered glass fraction of Experiment 6 we also found what appeared to be aragonite aggregates (using SEM–EDS). However, this could not be verified by bulk X-ray diffraction analyses and, thus, aragonite must be a minor component. Reactor sediments in Experiments 5 and 7 contain aragonite as the only identifiable crystalline substance. Amorphous materials include the silica in diatoms, biofilm material, organics, inadvertently included basaltic glass and possibly leached glass or palagonite.

Reactor sediments of the biotic experiments have a major element composition substantially different from those in the sterile experiment (Table 1). Much of the chemical inventory of these reaction products must be largely derived from basalt glass dissolution (Si, Ti, Al, Fe, Mn, P), because these elements are not sufficiently abundant in seawater (Table 1). Other elements may be derived from seawater or basalt (Mg, Ca, Na, K). Ti and Fe are particularly interesting because they are generally considered to be conservative, indicating how much of an original basaltic component is included in a particular substance. To evaluate the relative behavior of these elements, we presented our data in a basalt-normalized diagram (Fig. 4). In such a diagram, flat abundance patterns indicate that the corresponding elements are derived from basalt without relative fractionation, whereby the relative position of a pattern can be shifted to low values from dilution by addition of seawater-derived components. Upward shifts are possible by passive accumulation of insoluble basalt components while soluble components are removed. Positive anomalies above unity indicate uptake of this element from seawater. Negative anomalies indicate that a particular element is preferentially dissolved relative to the basalt inventory. In order to eliminate the interference from contamination with unaltered basalt fragments, we corrected the analyses by subtracting the maximum possible amount, 10% for Experiment 5, and 60% for Experiment 7; no correction was applied to Experiment 6. These corrections almost certainly over-correct for basalt, but these corrections do not change the abundance patterns much, even for Experiment 7, where the most dramatic corrections were applied.

The reactor sediment from sterile Experiment 6 shows a drastic depletion in Si, a flat pattern for

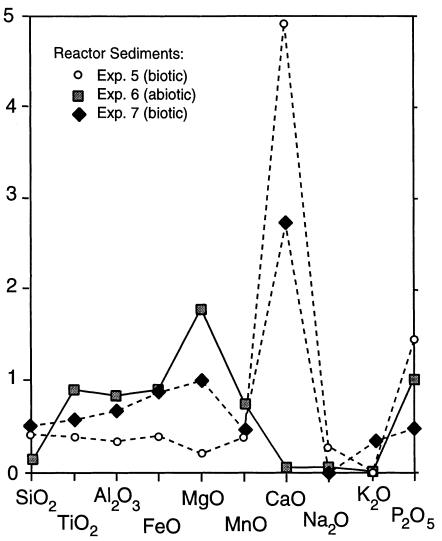

Fig. 4. Major element enrichment factors of reactor sediments relative to the unaltered basalt (all on a volatile-free basis, FeO reflects total iron). Note that the reactor sediment in the sterile experiment is enriched in Mg and highly depleted in Ca, while the biotic experiments are highly enriched in Ca.

Ti–Fe, Mn and P, significant enrichment in Mg and depletions in Ca, Na and K (Fig. 4). The low abundances of Ca, Na, and K show that basalt glass contamination must have been negligible and support the idea that there is very effective mobilization of these elements during abiotic glass dissolution.

The biotic Experiment 5 is the inoculated control to the sterile Experiment 6. It has the same starting materials and both were run in parallel, at the same time, temperature and light conditions. Experiment 7 is more difficult to compare without sterile experiment, in particular, because a different glass was used, it was run for a much longer time, and it included extended periods of darkness (see Table 1). The reactor sediment of Experiment 5 shows a flat abundance pattern from Si to Mn without Si depletion, minor depletion in Mg and a substantial addition of Ca from seawater. Na shows a slight depletion, K is almost entirely lost, and P appears to increase significantly relative to fresh basalt. The abundance pattern of the reactor sediment from Experiment 7 is somewhat intermediate between the ones of Experiments 5 and 6. The enrichment in Ca is less pronounced, and the pattern from Si to Mg shows a positive slope. There is a relative depletion of Si and a possible slight enrichment in Mg in Experiment 7 relative to Experiment 5. The chemical compositions of the biotic and the abiotic reactor sediments are very different from palagonite that shows characteristic enrichments in Ti and Fe and typically enrichments in K.

4.5. Other reaction products

Mineral deposition in the sterile Experiment 6 was apparent only in the reaction column. The biotic Experiments 5 and 7, however, produced significant quantities of solids in the water reservoir, in the settling chamber positioned in-line following the reactor, and in the Teflon tubing (Fig. 1). The latter provided a significant restriction to free flow, even though peristaltic pumps maintained constant flow rates throughout the entire duration of the experiment. These materials were dominated by aragonitic and siliceous (diatomaceous) materials that were often embedded in an algae mucus. Some of these organics were analyzed by microprobe, yielding very low totals from their high contents of organics. Their compositional variation is largely due to variable amounts of $CaCO_3$ or SiO_2 (Table 1). Mg was low in all sediments containing organisms. SEM observations reveal abundant diatoms in all materials recovered from both biotic experiments, even though bulk analyses suggest that there are fewer in Experiment 7. The reservoir sediment of Experiment 5 was recovered as a residue of a nitric-leach of the mucus from the bottom of the water reservoir (Table 1, Fig. 1). Its composition is quite similar to a natural diatomaceous ooze, with a relatively high K_2O but low CaO content (Table 1, Fig. 1).

4.6. $^{87}Sr/^{86}Sr$ isotopic data

We measured the $^{87}Sr/^{86}Sr$ for starting materials, altered glass, final reacted solution and reactor sediments (Table 2). The seawater used is identical to modern seawater and did not change in the course of the experiment. This reflects the experimental intention to dominate the solution with seawater Sr and adding basalt only as a minor component. The glass falls in the range of Loihi seamount tholeiites, while the $^{87}Sr/^{86}Sr$ ratios of altered glass and reactor sediments are intermediate between fresh basalt and

Table 2
Sr isotopic results from Experiments 5 and 6

Experiment	Sample type	Sr concentration (ppm)	$^{87}Sr/^{86}Sr$	Percentage seawater contribution
5/6	fresh glass	217.2	0.703672 ± 10	0
5/6	seawater	8	0.709184 ± 10	100
5	reacted water	n.d.	0.709193 ± 10	100
5	altered glass	213 [a]	0.703760 ± 10	1.60
6	altered glass	209 [a]	0.703715 ± 10	0.780
5	reactor sediment	6071	0.709114 ± 10	98.7
6	reactor sediment	24.78	0.708575 ± 9	89.0

n.d. = not determined.
[a] Measured by X-ray fluorescence [16], all other data by isotope dilution.

seawater. Given the constant $^{87}Sr/^{86}Sr$ in solution throughout the experiment, we can calculate mixing proportions of seawater and basalt Sr for each reaction product (Table 2). All altered glass samples have $^{87}Sr/^{86}Sr$ ratios higher than fresh basalt, and, thus, contain some quantities of seawater Sr. The altered glass in the biotic Experiment 5 (reactor sediment removed) contains about twice as much basaltic Sr than the abiotically altered glass (Table 2). Normalizing this result to experimental duration suggests that the rate of seawater Sr uptake in the biotically altered glass (Exp. 5) is actually 3–4 times higher than the abiotic experiment. Very large differences in Sr concentrations and isotope ratios can be found for the reactor sediments: the biotic reactor sediment contains 6071 ppm of Sr that is isotopically rather close to seawater, while the sterile reactor sediment has very little Sr (25 ppm) but with a more significant basalt component. However, the inventory of Sr in the biotic reactor sediment is very large, and the duration of the sterile experiment is longer than the biotic experiment. Taking these differences into account we estimate that the total mobilization rate of basaltic Sr in Experiment 5 is 40 times higher than in Experiment 6. It has to be noted here that the small difference in $^{87}Sr/^{86}Sr$ between seawater and the reaction product allows for a relatively large error in the estimate of its basaltic Sr inventory. Furthermore, we argued above that about 10% of the reactor sediment is made of basalt glass fragments, which also contributes some basaltic Sr. Assuming the worst possible combination of errors, the relative differences in mobilization rate are reduced to a factor of 20 times the abiotic rate.

5. Discussion: biological control of glass–seawater alteration

Several lines of evidence suggest that colonizing microbes are involved in the dissolution of glass. Etch pits, sponge textures, and the presence of DNA in microchannels in altered glass comprise physical evidence implicating microbial processes in glass alteration [5–7,13]. Experimental data support the hypotheses that bacteria cause etch pit formation in glass and that abiotic dissolution of glass does not produce etch pits [14]. Our current results provide further corroboration by showing that basalt glass alteration is accelerated when microbes are present. Sediment production rates were nearly doubled and there was a large basaltic Sr component in the reactor sediments when glass was altered in the presence of microbes. It is interesting to note that the high reaction rates in the presence of microbes are accompanied by relatively small mobilization rates of some major elements like Si. The low solution Si inventory in biotic experiments suggests that Si either remains in situ or precipitates or is utilized very soon after dissolution in biotic experiments. The abundant precipitation of secondary phases in biologically mediated glass (rock) dissolution will tend to isolate large portions of the oceanic crust from circulation, and thus ultimately limit chemical exchange between seawater and basalt. Thus, biologically active hydrothermal systems will tend to clog up faster than abiotic systems, and abiotic hydrothermal systems will deliver more Si to the oceans than biotic systems.

Our $^{87}Sr/^{86}Sr$ data also suggest that biological

processes enhance the addition of seawater Sr to the glass at least by a factor of three. This Sr either binds to the glass surface in a way that it cannot be removed as easily as in the abiotic case, or it is actually diffused into the glass, as it was observed for natural glasses [1]. Such a process is likely, because the formation of corrosion pits and microchannels into the glass enhances surface area and allows seawater Sr to penetrate into portions of the glass that are not easily removed during the physical separation of the reactor sediment. For these reasons we suggest that biological activity also enhances the uptake, and possibly the diffusion of Sr into fresh glass, even though this process still needs to be studied in detail.

The questions of how biological processes enhance glass dissolution and of how they accelerate the uptake of seawater Sr into glass remain poorly understood. It seems obvious that the local production of metabolic products may accelerate dissolution by changing pH and alter pH [3]. In fact, particular organic acids are much more effective in dissolving silicates than are inorganic acids of comparable strength. Thereby, dissolution rate appears to be directly related to the organic ligand concentration [19]. Such dissolution processes will be further enhanced by the expected roughing of the glass surface from the formation of etch pits and microchannels. One might further speculate that microbes produce enzymes that make it particularly easy to break up the glass structure and re-organize it into components that may be useful as nutrients. However, considering these complications, it seems quite clear that glass dissolution in nature cannot be simply explained as a congruent dissolution process, and that biology interferes with this process in many ways that are not completely understood.

One of the major results of this study is that microbes also play an important role in the fixation of dissolved components to in-situ produced (reactor) sediments, as well as in sediments produced outside the reactor: abiotic alteration retains a series of insoluble components of the glass (Ti, Al, Fe) and significant quantities of Mg out of seawater to produce a stable silicate layer (pyroaurite). Si, Ca, Na and K are effectively not used in this reaction, and they are lost to solution. In the biotic experiments, aragonite is one of the major reaction products, whereby substantial quantities of Ca are also removed from seawater. Furthermore, both biotic experiments show abundant diatoms that apparently utilize basaltic Si for the formation of their tests. Reactor sediments also contain significant quantities of basaltic Ti, Al, Fe and Mg, suggesting that there must be a (residual?) phase containing these, in part very insoluble, elements. However, the major effects are the inverse chemical behavior of Mg and Ca in the abiotic and biotic reactor sediments.

A comparison of Experiments 5 and 7 may be used to gain some insights into the role of light in our experiments, even though experimental conditions were not optimized to address this particular problem. Overall, the solution data suggest that Si utilization continues through the entire period of darkness. This would suggest that (photoautotrophic) Si utilization by green algae may not be the dominant process and that there may be other means to utilize Si. Alternatively, biofilm development may disturb the dissolution–precipitation behavior, even though this appears unlikely because biofilms are relatively thin and discontinuous. The Ca enrichment in reactor sediments from Experiment 7 is not nearly as pronounced as in Experiment 5. This may indicate that darkness may have caused some dissolution of aragonite, a behavior that is quite characteristic for the day/night cycle of *Halimeda* [17]. Furthermore, the pattern of major elements in the reactor sediment of Experiment 7 is somewhat intermediate between the pattern for Experiments 5 and 6 (Fig. 4). This may indicate that some of the extreme chemical differences between biotic and abiotic experiments (in particular the enrichment in Ca) may be due to the presence of light throughout Experiment 5 and in the early phase of Experiment 7.

These observations show that microbial activity has an effect on glass alteration, with respect to the types of alteration as well as its kinetics. This is corroborated by petrographic observations of glasses from many geological settings [3–7] and it is likely that all low-temperature alteration of volcanic glass in nature is influenced and possibly controlled by microbial activity. From a global mass-balance point of view, these processes play an important role in oceanic crust alteration [1], and when volcanic ash is immersed in seawater and deposited on the ocean floor as a volcaniclastic sediment. We estimate that

off-axis volcanic glass production is at least the same as the Mid-Ocean Ridge rates. The recent eruption of Mt Pinatubo (10 km^3 of ash) and the 1815 eruption of Tambora (100–300 km^3) alone suggest that the total production of glass from arc eruptions is probably in excess of 1 km^3/a. This roughly doubles the ocean crustal rate to about $0.5 * 10^{16}$ g (glass) per year.

These estimates are crude, but they underscore the potential of significant geochemical fluxes from these processes. These fluxes are likely to be modulated by biological evolution and the intensity of volcanism over geological time. The biggest change should have occurred at the transition from an abiotic to a biotic earth, early in its history, and during geological periods which are characterized by unusually large production rates of volcanic material (the Cretaceous?). Thus, fluxes from microbial mediation of volcanic glass alteration should have been highly non-linear through geological history. However, these variations ultimately need to be quantified if we are to understand the isotopic variation of seawater back through geological time, in particular the $^{87}Sr/^{86}Sr$ ratio and also the $^{143}Nd/^{144}Nd$ ratio. Even though there is evidence that biologically mediated glass alteration influences chemical inventories and cycles in the oceans, at least during specific geological times, not much can be said yet about their absolute fluxes. Understanding of these global processes would be greatly helped by improved estimates of volcaniclastic abundances and experimental evaluations of the bulk chemical fluxes involved in glass alteration in a biologically active environment.

6. Concluding remarks

Our study provided evidence that biological activity substantially accelerates the chemical exchange between volcanic glass and seawater, and that the reaction products differ markedly between biologically mediated and sterile conditions. This suggests that biological activity plays important qualitative and quantitative roles in the exchange of chemical elements between hydrosphere and lithosphere. Many questions remain and need to be addressed before the process of biologically mediated alteration of volcanic glass and its effects on global chemical fluxes can be understood: Which metabolic reactions promote the dissolution of glass? Which reactions control the precipitation of the dissolved components? What is the role of heterotrophic versus chemo-autotrophic microbes? Which microbes take part in dissolution and which ones in precipitation reactions? Is there an influence of microbial community structure on glass alteration processes? What is the role of temperature, light, and oxygen fugacity, on microbial mediation of silicate dissolution? While we could add to the increasing recognition that microbial processes play an important role in water–rock interaction, we also appear to have opened the door to many new questions.

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